



US008974762B2

(12) **United States Patent**  
**Ergang et al.**

(10) **Patent No.:** **US 8,974,762 B2**  
(45) **Date of Patent:** **Mar. 10, 2015**

(54) **SILICA PARTICLE MANUFACTURING PROCESS**

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(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 458 days.

(21) Appl. No.: **13/269,159**

(22) Filed: **Oct. 7, 2011**

(65) **Prior Publication Data**

US 2013/0036946 A1 Feb. 14, 2013

**Related U.S. Application Data**

(63) Continuation-in-part of application No. 12/756,526, filed on Apr. 8, 2010.

(51) **Int. Cl.**

**C01B 33/02** (2006.01)  
**C01F 7/00** (2006.01)  
**C01B 33/12** (2006.01)  
**C01B 33/141** (2006.01)  
**C01B 33/18** (2006.01)  
**C09C 1/02** (2006.01)  
**C09C 1/30** (2006.01)  
**C01B 33/187** (2006.01)

(52) **U.S. Cl.**

CPC ..... **C01B 33/12** (2013.01); **C01B 33/1415** (2013.01); **C01B 33/18** (2013.01); **C09C 1/02** (2013.01); **C09C 1/3081** (2013.01); **C01B 33/187** (2013.01); **C01P 2002/54** (2013.01); **C01P 2006/12** (2013.01); **C01P 2006/14** (2013.01); **C01P 2006/16** (2013.01)  
USPC ..... **423/349**; **423/600**

(58) **Field of Classification Search**

CPC ..... **C01B 33/12**; **C01B 33/18**; **C01B 33/141**; **C01B 33/187**; **C01B 33/1415**; **C01B 33/1417**; **C01B 33/149**; **C01P 2006/12**; **C01P 2006/14**; **C01P 2006/16**; **C01P 2006/54**; **C09C 1/02**; **C09C 1/3081**  
USPC ..... **423/335–340**, **600**  
See application file for complete search history.

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(57) **ABSTRACT**

Methods of forming a silica-containing products are disclosed. One method comprises: (a) providing a silica containing precursor (SCP) contained in solution that has a pH less than or equal to a pH of 7; (b) optionally doping the SCP with one or more metal species; (d) adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to 4 mS; (e) optionally filtering and drying the SCP; and (f) optionally reacting the dried product from step e with a functional group. Another method comprises: (a) providing a silica containing precursor (SCP) contained in solution that has a pH greater than 7; (b) adjusting the pH of the solution to less than or equal to 7; (c) optionally doping the SCP with one or more metal species; (d) adjusting the pH of the solution to greater than 7; and (e) adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to 4 mS; (f) optionally filtering and drying the SCP. The SCP is then added to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a substrate selected from hydrated alkaline earth oxide, lanthanide oxide, and combinations thereof.

**16 Claims, No Drawings**



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## SILICA PARTICLE MANUFACTURING PROCESS

### CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation in part application of U.S. patent application Ser. No. 12/756,526, "Silica Particle Manufacturing Process," filed on Apr. 8, 2010, which is incorporated herein by reference in its entirety.

### FIELD OF THE INVENTION

This disclosure pertains to methods of manufacture for silica-containing compositions. The invention has particular relevant to such compositions comprising a hygroscopic solid such that the resulting product comprises a silica-containing product deposited on a substrate of hydrated alkaline earth oxide or lanthanide oxide.

### BACKGROUND OF THE INVENTION

Silica-containing materials have ubiquitous applications. More specifically, a variety of manufacturing processes that produce either consumer or industrial products utilize silica-containing materials for various purposes. For example, silica-containing products can be utilized as fillers in coatings (e.g. paints) and polymer composites, catalysts supports, beer/wine/juice clarifiers. New methods of manufacture are also desired by the industry.

### SUMMARY OF THE INVENTION

The present invention provides for a method of forming a silica-based product comprising: a. providing a silica containing precursor (SCP) contained in solution that has a pH less than or equal to a pH of about 7; b. optionally doping the SCP with one or more metal species, wherein said doping occurs when the solution has a pH less than or equal to a pH of about 7; c. adjusting the pH of the solution to greater than about 7; d. adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to about 4 millisiemens (mS), wherein said addition occurs prior to, simultaneous with, or after the pH adjustment in step 1c; e. optionally filtering and drying the SCP; f. optionally reacting the dried product from step e with a functional group and optionally wherein the resultant functionalized dried product is at least one of the following: a functionalized metal oxide-doped or metal sulfide-doped silica-containing product; and g. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

The present invention also provides for a method of forming a silica-based product comprising: a. providing a silica containing precursor (SCP) contained in solution that has a pH greater than 7; b. adjusting the pH of the solution to less than or equal to 7; c. optionally doping the SCP with one or more metal species, wherein said doping occurs when the solution has a pH less than or equal to a pH of 7; d. adjusting the pH of the solution to greater than 7; e. adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to 4 mS, wherein said addition occurs prior to, simultaneous with, or after the pH adjustment in step 2d; f. optionally filtering and drying the SCP; g. optionally reacting the dried product from step f with a functional group and optionally wherein the resultant functional-

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ized dried product is at least one of the following: a functionalized metal oxide-doped or metal sulfide-doped silica product; and h. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

The present invention also provides for a method of forming a silica-containing product comprising a. providing a silica containing precursor (SCP) contained in solution that has a pH less than or equal to a pH of about 7; and b. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

The present invention also provides for a method of forming a silica-containing product comprising a. providing a silica-containing precursor (SCP) contained in solution that has a pH greater than a pH of about 7; and b. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

### DETAILED DESCRIPTION OF THE INVENTION

As stated above, the silica-containing products encompassed by this invention can be made by the following methods.

One methodology involves starting from an acidic starting point.

In one embodiment, the method comprises forming a silica-containing product comprising the steps of a. providing a silica-containing precursor (SCP) contained in solution that has a pH less than or equal to a pH of about 7; b. optionally doping the SCP with one or more metal species, wherein said doping occurs when the solution has a pH less than or equal to a pH of about 7; c. adjusting the pH of the solution to greater than 7; d. adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to about 4 mS, wherein said addition occurs prior to, simultaneous with, or after the pH adjustment in step 1c; e. optionally filtering and drying the SCP; f. optionally reacting the dried product from step e with a functional group and optionally wherein the resultant functionalized dried product is at least one of the following: a functionalized metal oxide-doped or metal sulfide-doped silica product; and g. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

In all embodiments, adding the SCP to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a substrate selected from hydrated alkaline earth oxide, lanthanide oxide, and combinations thereof.

In another embodiment, the functional group in step f is an organosilane.

In another embodiment, the silicon-containing precursor is selected from at least one of the following: silicic acid, colloidal silica, tetraethylorthosilicate, and dispersed fumed silica.

In another embodiment, the pH range of the SCP in step 1(a) is from of about 3 to about 4.



In another embodiment, the pH of the SCP is adjusted to greater than about 7 by mixing said SCP with an alkaline solution at a shear rate of about 6 to about 23 m/s based on tip speed.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than about 7 by mixing said SCP with an alkaline solution via a mixing chamber. An example of a mixing chamber is described in U.S. Pat. No. 7,550,060, "Method and Arrangement for Feeding Chemicals into a Process Stream." This patent is herein incorporated by reference. In one embodiment, the mixing chamber comprises a first conduit having one or more inlets and outlets; a second conduit having one or more inlets and outlets, wherein said first conduit secures to said second conduit and traverses said second conduit; a mixing chamber that has one or more inlets and outlets, wherein said second conduit secures to said mixing chamber and wherein said outlets of said first conduit and said outlets of said second conduit are in communication with said mixing chamber; and an adaptor that is in communication with said outlet of said mixing chamber and is secured to said mixing chamber. The mixing chamber can then be attached or in communication with a receptacle that holds/processes through (e.g. a conduit) a mixed product. In one embodiment, said mixing chamber can then be attached or in communication with a receptacle that holds/processes a mixed product resulting from said pH adjustment of said SCP.

Additionally, Ultra Turax, Model Number UTI-25 (available from IKA® Works, Inc. in Wilminaton, N.C.), a mixing device, can be utilized. It is envisioned that any suitable reactor or mixing device/chamber may be utilized in the method of the invention.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than about 7 by combining said SCP with an alkaline solution with mixing yielding a Reynolds Number greater than or equal to 2,000, to form the silica-containing product.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than about 7 by combining said SCP with an alkaline solution under transitional flow conditions (i.e., Reynolds Numbers between 2,000 and 4,000) to form the silica-containing product.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than about 7 by combining said SCP with an alkaline solution under turbulent flow conditions (i.e., Reynolds Numbers greater than or equal to 4,000) to form the silica-containing product.

In another embodiment, the pH of the SCP is adjusted to a pH range of about 7 to about 11 with the use of a chemistry selected from at least one of the following: ammonium hydroxide, ammonium carbonate, mineral bases such as but not limited to sodium hydroxide and/or potassium hydroxide, organic bases such as but not limited to trimethylammonium hydroxide, alkaline silicates, sulfide salts such as but not limited to sodium sulfide, and polysulfide containing salts such as but not limited to calcium polysulfide and/or sodium polysulfide.

In another embodiment, the resulting slurry from step d is filtered and dried such that the solid concentration of said dried and filtered product is increased from about 5 wt % to about 99 wt %.

In another embodiment, the dried product from step e is surface treated with an organosilane via controlled hydrolysis and condensation of the silane to the silica surface in an organic solvent, supercritical solvent, or solvent-free process.

In another embodiment, the aqueous-based SCP is added to a hygroscopic solid such that the resulting product comprises

a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

In another embodiment, the method comprises forming a silica-containing product comprising a. providing a silica containing precursor (SCP) contained in solution that has a pH less than or equal to a pH of 7; and b. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

In embodiments, the aqueous-based SCP is added to a hygroscopic inorganic solid in a. fluidized bed mixer such that the water is adsorbed uniformly by the solid to form a hydrated powder containing the SCP. A fluidized bed mixer is a mixer wherein a dry powder is fluidized via mechanical or pneumatic means to allow for thorough and complete mixing with a solution or another dry powder. Examples of said fluidized bed mixer include but are not limited to a plow mixer, screw mixer, or a ribbon mixer.

Another methodology involves starting from an alkaline starting point.

In one embodiment, the method comprises forming a silica-containing product comprising the steps of: a. providing a silica-containing precursor (SCP) contained in solution that has a pH greater than about 7; b. adjusting the pH of the solution to less than or equal to about 7; c. optionally doping the SCP with one or more metal species, wherein said doping occurs when the solution has a pH less than or equal to a pH of about 7; d. adjusting the pH of the solution to greater than about 7; e. adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to about 4 mS, wherein said addition occurs prior to, simultaneous with, or after the pH adjustment in step 2d; f. optionally filtering and drying the SCP; g. optionally reacting the dried product from step f with a functional group and optionally wherein the resultant functionalized dried product is at least one of the following: a functionalized metal oxide-doped or metal sulfide-doped silica-containing product; and h. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

In all embodiments, adding the SCP to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a substrate selected from hydrated alkaline earth oxide, lanthanide oxide, and combinations thereof.

In another embodiment, the functional group in step f is an organosilane.

In another embodiment, the functional group in step g is an organosilane.

In another embodiment, the silicon-containing precursor is selected from at least one of the following: silicic acid, colloidal silica, tetraethylorthosilicate, alkaline silicates, and dispersed fumed silica.

In another embodiment, the pH of the silicon-containing precursor is adjusted through the use of at least one of the following: carbonic acid, an organic acid(s) such as but not limited to acetic acid, a mineral acid(s) such as but not limited to sulfuric acid and/or hydrochloric acid such that the pH is decreased to a range of from to about 2 to about 7.

In another embodiment, the pH range of the SCP is adjusted to a range of about 3 to about 4 with acetic acid.

In another embodiment, the pH of the SCP is adjusted to a pH range of about 7 to about 11 with the use of a chemistry selected from at least one of the following: ammonium



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hydroxide, ammonium carbonate, mineral bases, organic bases, alkaline silicates, sulfide salts, and polysulfide containing salts.

In another embodiment, the resulting slurry from step e is filtered and dried such that the solid concentration of said dried and filtered product is increased from about 5 wt % to about 99 wt %.

In another embodiment, the dried product from step f is surface treated with an organosilane via controlled hydrolysis and condensation of the silane to the silica surface in an organic solvent, supercritical solvent, or solvent-free process.

In another embodiment, the aqueous-based SCP is added to a hygroscopic solid such that the resulting product comprises a metal oxide-doped or metal sulfide-doped silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

In another embodiment, the method comprises forming a silica-containing product comprising a. providing a silica-containing precursor (SCP) contained in solution that has a pH above a pH of 7; and b. adding the aqueous-based SCP to a hygroscopic solid such that the resulting product comprises a silica-containing product deposited on a hydrated alkaline earth oxide or lanthanide oxide substrate.

In embodiments, the aqueous-based SCP is added to a hygroscopic inorganic solid in a fluidized bed mixer such that the water is adsorbed uniformly by the solid to form a hydrated powder containing the SCP. A fluidized bed mixer is a mixer wherein a dry powder is fluidized via mechanical or pneumatic means to allow for thorough and complete mixing with a solution or another dry powder. Examples of said fluidized bed mixer include but are not limited to a plow mixer, screw mixer, or a ribbon mixer.

In another embodiment, the pH of the SCP is adjusted to greater than about 7 by mixing said SCP with an alkaline solution at a shear rate of about 6 to about 23 m/s based on tip speed.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than 7 by mixing said SCP with an alkaline solution via a mixing chamber. An example of a mixing chamber is described in U.S. Pat. No. 7,550,060, "Method and Arrangement for Feeding Chemicals into a Process Stream," This patent is herein incorporated by reference. In one embodiment, the mixing chamber comprises a first conduit having one or more inlets and outlets; a second conduit having one or more inlets and outlets, wherein said first conduit secures to said second conduit and traverses said second conduit; a mixing chamber that has one or more inlets and outlets, wherein said second conduit secures to said mixing chamber and wherein said outlets of said first conduit and said outlets of said second conduit are in communication with said mixing chamber; and an adaptor that is in communication with said outlet of said mixing chamber and is secured to said mixing chamber. The mixing chamber can then be attached or in communication with a receptacle that holds/processes through (e.g. a conduit) a mixed product. In one embodiment, said mixing chamber can then be attached or in communication with a receptacle that holds/processes a mixed product resulting from said adjustment of said SCP.

Additionally, Ultra Turax, Model Number UTI-25 (available from IKA® Works, Inc. in Wilmington, N.C.), a mixing device, can be utilized. It is envisioned that any suitable reactor or mixing device/chamber may be utilized in the method of the invention.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than 7 by combining

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said SCP with an alkaline solution with mixing yielding a Reynolds Number greater than or equal to 2000, to form the silica based product.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than about 7 by combining said SCP with an alkaline solution under transitional flow conditions (i.e., Reynolds Numbers between 2,000 and 4,000) to form the silica-containing product.

In another embodiment, the method further comprises adjusting the pH of the SCP to greater than about 7 by combining said SCP with an alkaline solution under turbulent flow conditions (i.e., Reynolds Numbers greater than or equal to 4,000) to form the silica-containing product.

The invention further provides for a composition in which the silica-containing precursor is agglomerated with a metal oxide dopant such that the final discrete silica-containing particle contains a homogeneous dispersion of metal oxide particles in a high surface area, high pore volume structure. The homogeneous dispersion of discrete metal oxide particles throughout the silica-containing particle framework, is expected to provide more reactive surface area for a given metal oxide than a neat metal oxide particle.

The sulfur-based species of the present invention may be selected from a representative list but not intended to be a limiting list of at least one of the following: sulfide salts, dithiocarbamates, polymer-based dithiocarbamates, and polysulfide salts. Sulfide salts maybe but not limited to sodium sulfide, potassium sulfide, and/or metal sulfides such as copper sulfide. Dithiocarbamates may be but not limited to dimethyldithiocarbamate (DMDTC) or diethyldithiocarbamate (DEDTC). Polymer-based dithiocarbamates contain organic polymers containing the functional group  $R_nCS_2$ , wherein R is an alkyl group which is linear or branched. An example of a commercially available polymer-based dithiocarbamate is described in U.S. Pat. Nos. 5,164,095 and 5,346,627, which are herein incorporated by reference. Polysulfides that can be used in the present invention include, but are not limited to, sodium polysulfide and calcium polysulfide.

Organosilanes that can be used in the current invention are well known in the art and may be represented generally by  $R_{(4-a)}SiX_a$ , wherein a may be from 1 to 3. The organofunctional group, R—, may be any aliphatic or alkene containing functionalized group such as propyl, 3-chloropropyl, amine, thiol, and combinations thereof. X is representative of a hydrolysable alkoxy group, typically methoxy or ethoxy. Some examples are 3-thiopropyl and mercaptopropyl silanes.

During the preparation of the composition of this invention, salt is added to increase the conductivity of the reaction solution to about 4 mS. Examples of the salts that can be used include, but are not limited to, alkali and alkaline halides, sulfates, phosphates, and nitrates such as sodium sulfite, potassium chloride, sodium chloride, sodium nitrate, calcium sulfate, and potassium phosphate. One skilled in the art would recognize that the effective amount of salt added to reach the desired conductivity will vary dependent on the salt of choice.

Thiols and amines are represented generally by the class of organic and inorganic compounds containing the amine or thiol group having the general formula  $-B-(SH)$  or  $-B-(NH_2)$ , wherein B is a linear or branched group consisting of carbon atoms such as wherein n is from 1 to 15, in particular where n is 1 to 6, and most preferred where n is 3.

Examples of hygroscopic solids (e.g., anhydrous inorganic hygroscopic solids) that can be used in this invention include, but are not limited to, alkali oxides, alkaline earth oxides, lanthanide oxides, the like, and combinations thereof. Specific examples include calcium sulfate, magnesium sulfate, ammonium sulfate, alkali hydroxides, the like, and combina-



tions thereof it should be appreciated that one skilled in the art would recognize that the effective amount of solid needed to reach the desired dryness will vary dependent on the solid of choice, in embodiments, the hygroscopic inorganic solid is at least one alkaline earth oxide or lanthanide oxide. Specific examples used herein are intended to encompass such variations.

#### Example 1

In this example, 2180 g of 7 wt % silicic acid was added to a heel containing 450 g deionized (DI) water and 150 g of silicic acid heated to 90° C. The silicic acid was fed at 10 ml/mm for 3 h via a peristaltic pump into a 5 L reaction flask.

A solution containing 16.4 g of 2.5 wt % ammonia solution and 5.84 g ammonium carbonate was prepared in 24.6 g DI water. The solution was added to the reaction flask quickly whereupon the viscosity of the solution increased significantly. The mixture was stirred for 30 minutes, then any remaining silicic acid was fed at 20 ml/min. Upon completion of the silicic acid feed, the heating was turned off and the solution was allowed to cool.

The silica slurry was filtered and freeze-dried at 150° C. to produce a dry powder. Nitrogen sorption analysis of the powder was performed on an Autosorb-1C unit from Quantachrome. The sample was degassed at 300° C. for 2 h, then characterized by a multi-point BET surface area, total pore volume, and BJH (Barrett-Joyner-Halenda) adsorption pore size distribution. Physical data indicated a surface area of 354 square meters per gram, a pore volume of 1.19 cc/g, and a pore diameter of 13.5 nm.

#### Example 2

In this example, three solutions were prepared: A) 100 g Nalco N8691 silica sol, B) 3 g glacial acetic acid dissolved in 50 g DI water, and C) 2.7 g ammonium carbonate and 7.5 g 25 wt % ammonia dissolved in 150 g DI water. Solution B was added to solution A, followed by subsequent addition of solution C at a high shear rate. The mixture was stirred for 1-2 minutes before filtration. Nalco N8691 can be obtained from Nalco Company, 1601 West Diehl Road, Naperville, Ill. 60563.

The silica slurry was filtered and dried at 300° C. to produce a dry powder. Nitrogen sorption analysis was performed on an Autosorb-1C unit from Quantachrome. The sample was degassed at 300° C. for 2 h, then characterized by a multi-point BET surface area, total pore volume, and BJH adsorption pore size distribution. Nitrogen sorption analysis indicated a surface area of 240 square meters per gram, a pore volume of 0.57 cc/g, and a pore diameter of 9.6 nm.

#### Example 3

In this example, three solutions were prepared: A) 100 g Nalco N8691 silica sol, B) 3 g glacial acetic acid and 11.8 g polyaluminum chloride dissolved in 50 g DI water, and C) 15 g of 25 wt % ammonia dissolved in 150 g DI water. Solution B was added to solution A with mixing, followed by subsequent addition of solution C at a high shear rate. The mixture was stirred for 1-2 minutes before filtration.

The Al-doped silica slurry was filtered and dried at 300° C. to produce a dry powder, followed by nitrogen sorption analysis performed on an Autosorb-1C unit from Quantachrome. The sample was degassed at 300° C. for 2 h, then characterized by a multi-point BET surface area, total pore volume, and BJH adsorption pore size distribution. Nitrogen sorption

analysis indicated a surface area of 469 square meters per gram, a pore volume of 0.82 cc/g, and a pore diameter of 7.0 nm.

#### Example 4

In this example, three solutions were prepared: A) 25 g Nalco N8691 silica sol, B) 12.45 g copper sulfate and 3 g glacial acetic acid dissolved in 200 g DI water, and C) 39.5 g calcium polysulfide solution and 7.5 g 25 wt % ammonia dissolved in 200 g DI water. Solution B was added to solution A, followed by subsequent addition of solution C at a high shear rate. After mixing, 425 g of DI water was added at a high shear rate. The mixture was stirred for 1-2 minutes. 37.6 g of aqueous slurry was sprayed onto 56.1 g of CaO with a spray bottle while stirring in a round bottom flask.

Nitrogen sorption analysis of the powder was performed on an Autosorb-1C unit from Quantachrome. The sample was degassed at 150° C. for 6 h, then characterized by a multi-point BET surface area, total pore volume, and BJH adsorption pore size distribution. Nitrogen sorption analysis indicated a surface area of 20.4 square meters per gram, a pore volume of 0.18 cc/g, and a pore diameter of 34.7 nm. TGA analysis of the powder indicated 3.8 wt % mass loss due to moisture.

#### Example 5

In this example, 500 ml of sodium silicate solution, which was diluted with DI water to approximately 8 wt % silica, was desalted by running through an ion exchange column filled with 250 ml of acidic Dowex 650C resin. The solution coming out from the column was collected at pH value between 3 and 3.5 containing 7.6 wt % of solid. 39.83 g of aqueous acid sol was sprayed onto 56.0 g of CaO with a spray bottle while stirring in a round bottom flask to yield a final dry-flowing powder.

Nitrogen sorption analysis of the powder was performed on an Autosorb-1C unit from Quantachrome. The sample was degassed at 180° C. for 5 h, and then characterized by a multi-point BET surface area, total pore volume, and BJH adsorption pore size distribution. Nitrogen sorption analysis indicated a surface area of 26.4 square meters per gram, a pore volume of 0.12 cc/g, and a pore diameter of 17.5 nm, TOA analysis of the powder indicated 15.8 wt % mass loss due to moisture.

### COMBINATIONS OF COMPONENTS DESCRIBED IN PATENT APPLICATION

In one embodiment, the composition of matter claims include various combinations of sorbent components and associated compositions, such molar ratios of constituent particles. In a further embodiment, the claimed compositions include combinations of the dependent claims. In a further embodiment, a range or equivalent thereof of a particular component shall include the individual component(s) within the range or ranges within the range.

In another embodiment, the method of use claims include various combinations of the sorbent components and associated compositions, such molar ratios of constituent particles. In a further embodiment, the claimed methods of use include combinations of the dependent claims. In a further embodiment, a range or equivalent thereof of a particular component shall include the individual component(s) within the range or ranges within the range.



In another embodiment, the method of manufacture claims include various combinations of the sorbent components and associated compositions, such as pH control. In a further embodiment, the claimed methods of use include combinations of the dependent claims. In a further embodiment, a range or equivalent thereof of a particular component shall include the individual component(s) within the range or ranges within the range.

All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While this invention may be embodied in many different forms, there are described in detail herein specific preferred embodiments of the invention. The present disclosure is an exemplification of the principles of the invention and is not intended to limit the invention to the particular embodiments illustrated. In addition, unless expressly stated to the contrary, use of the term "a" is intended to include "at least one" or "one or more." For example, "a device" is intended to include "at least one device" or "one or more devices."

Any ranges given either in absolute terms or in approximate terms are intended to encompass both, and any definitions used herein are intended to be clarifying and not limiting. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all subranges (including all fractional and whole values) subsumed therein.

Furthermore, the invention encompasses any and all possible combinations of some or all of the various embodiments described herein. Any and all patents, patent applications, scientific papers, and other references cited in this application, as well as any references cited therein, are hereby incorporated by reference in their entirety. It should also be understood that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications can be made without departing from the spirit and scope of the invention and without diminishing its intended advantages. It is therefore intended that such changes and modifications be covered by the appended claims.

The claimed invention is:

1. A method of forming a silica-containing product, the method comprising:

- a. providing a silica-containing precursor (SCP) contained in solution;
- b. doping the SCP with one or more metal species;
- c. optionally adjusting the pH of the solution to greater than about 7 or less than about 7;
- d. adding an effective amount of salt to the solution so that the conductivity of the solution is greater than or equal to about 4 mS, wherein said addition occurs prior to, simultaneous with, or after the pH adjustment in step c;
- e. optionally filtering and drying the SCP;
- f. optionally reacting the dried product from step e with a functional group wherein the resultant functionalized dried product is at least one of the following: a functionalized metal oxide-doped or metal sulfide-doped silica-containing product; and
- g. adding the SCP to a hygroscopic solid such that the resulting product comprises the metal oxide-doped or metal sulfide-doped silica-containing product deposited

on a substrate selected from hydrated alkaline earth oxide, lanthanide oxide, and combinations thereof.

2. The method of claim 1, comprising providing a silica-containing precursor (SCP) contained in solution wherein the pH value is less than or equal to a pH of about 7.

3. The method of claim 1, comprising providing a silica-containing precursor (SCP) contained in solution wherein the pH value is greater than a pH of about 7.

4. The method of claim 1, wherein the functional group in step f is an organosilane.

5. The method of claim 1, wherein the silica-containing precursor is at least one of the following: silicic acid, colloidal silica, tetraethylorthosilicate, alkaline silicates, dispersed fumed silica, and combinations thereof.

6. The method of claim 1, wherein the pH of the silica-containing precursor is adjusted through the use of at least one of the following: carbonic acid, organic acids, mineral acids, and combinations thereof such that the pH is decreased to a range of from 2 to 7.

7. The method of claim 1, wherein the pH range of the SCP in step (a) is from 3 to 4.

8. The method of claim 7, wherein the pH range of the SCP is adjusted to a range from about 3 to about 4 with acetic acid.

9. The method of claim 1, wherein the SCP is heated to a temperature range of from 25° C. to 95° C.

10. The method of claim 1, wherein the pH of the SCP is adjusted to a pH range from about 7 to about 11 with the use of a chemical selected from at least one of the following: ammonium hydroxide, ammonium carbonate, mineral bases, organic bases, alkaline silicates, sulfide salts, organic dithiocarbamates, polymer-based dithiocarbamates, polysulfide containing salts, and combinations thereof.

11. The method of claim 1, wherein the pH of the SCP is adjusted to greater than about 7 by mixing said SCP with an alkaline solution at a shear rate of about 6 to about 23 m/s based on tip speed.

12. The method of claim 1, wherein the resulting slurry from step d is filtered and dried such that the solid concentration of said dried and filtered product is increased from about 5 wt % to about 99 wt %.

13. The method of claim 1, further comprising wherein the dried product is surface treated with an organosilane via controlled hydrolysis and condensation of the silane to the silica surface in at least one of the following: organic solvent, supercritical solvent, solvent-free process, and combinations thereof.

14. The method of claim 1, wherein the SCP is added to a hygroscopic solid such that the water is adsorbed uniformly by the solid to form a hydrated powder containing the SCP.

15. The method of claim 1, wherein the pH of the SCP is adjusted to greater than about 7 by mixing said SCP with an alkaline solution via a mixing chamber; and optionally wherein the mixing chamber comprises a first conduit having one or more inlets and outlets; a second conduit having one or more inlets and outlets, wherein said first conduit secures to said second conduit and traverses said second conduit; a mixing chamber that has one or more inlets and outlets, wherein said second conduit secures to said mixing chamber and wherein said outlets of said first conduit and said outlets of said second conduit are in communication with said mixing chamber; and an adaptor that is in communication with said outlet of said mixing chamber and is secured to said mixing chamber; and said mixing chamber can then be attached or in communication with a receptacle that holds/processes a mixed product resulting from said pH adjustment of said SCP.

16. The method of claim 1, wherein SCP is added to a hygroscopic inorganic solid uniformly via a fluidized bed mixer, wherein a dry powder is fluidized via mechanical or pneumatic means to allow for thorough and complete mixing with a solution or another dry powder.

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